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Variations in quadrupole splitting of the ^{57}Fe in the M1 and M2 sites of meteoritic olivines with different origin

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Abstract A comparative study of meteoritic olivine in bulk samples of Farmington L5 and Tsarev L5 ordinary chondrites and extracted from Omolon and Seymchan the main-group pallasites was performed using Mössbauer spectroscopy with a high velocity resolution. Mössbauer spectra for each specimen were measured at 295 and 90 K. Mössbauer spectral components related to the ^{57}Fe in crystallographically non-equivalent sites M1 and M2 in olivines were determined and their Mössbauer hyperfine parameters were evaluated. It was found small variations of quadrupole splitting for the ^{57}Fe in both the M1 and M2 sites of olivines in bulk ordinary chondrites and olivines extracted from pallasites.

Keywords Mössbauer spectroscopy · Quadrupole splitting · Meteorites · Olivine

1 Introduction

Olivine $(Fe, Mg)_2SiO_4$ is a widely-spread rock-forming mineral in terrestrial and extraterrestrial matter. Olivine contains two crystallographically non-equivalent six-fold octahedral sites for Fe^{2+} and Mg^{2+} denoted as M1 and M2. These sites in olivine are occupied by Fe^{2+} and Mg^{2+} ions in different ways. The iron state in both sites of olivine with different origin is of interest because it may contain information about possible variations in the iron environment related to the olivine origin. Mössbauer spectroscopy was successfully applied for study various olivines. Studies of natural

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(terrestrial) and synthetic olivines demonstrated the presence of two quadrupole doublets in Mössbauer spectra which were related to the ^{57}Fe in the M1 and M2 sites [1–4]. However, in the case of olivine in bulk meteorites the Mössbauer spectra of various meteorites were fitted using one quadrupole doublet for olivine component (see, for instance, [5, 6]). Application of Mössbauer spectroscopy with a high velocity resolution in meteorite studies showed some new results which were not possible to obtain from the spectra measured with a low velocity resolution using conventional spectrometers [7–9]. In the present work we consider the results of comparative study of the iron state in the M1 and M2 sites of olivines in two bulk ordinary chondrites and olivines extracted from two pallasites using Mössbauer spectroscopy with a high velocity resolution at 295 and 90 K.

2 Experimental

Fragments of the Tsarev L5 and Farmington L5 equilibrated ordinary chondrites were used for preparation of powdered samples of the bulk meteorites. Fayalite (Fa or Fe_2SiO_4) content in olivine was 24.3 % (Tsarev L5) [10] and 23 % (Farmington L5) [11]. Olivine samples were mechanically extracted from fragments of the Omolon and Seymchan the main-group pallasites and powdered with removing of magnetic fraction remains using magnet. Fa content in olivine was 12.3 % (Omolon) [12] and 11.3 % (Seymchan) [13]. Chondrites and olivine powders were glued on aluminum foil free from iron with diameter of 2 cm. The thickness of the samples was within the limit of thin absorber. Meteorite powders were analyzed by X-ray diffraction using X'Pert PRO MRD diffractometer with CuK_α radiation for the phase control.

Mössbauer spectra were measured using an automated precision Mössbauer spectrometric system built on the base of the SM-2201 spectrometer with a saw-tooth shape velocity reference signal formed using 4096 bits. Details and characteristics of this spectrometer and the system were given elsewhere [14, 15]. The Mössbauer spectra were measured in transmission geometry with moving absorber in the cryostat at 295 and 90 K and recorded in 4096 channels. The 1.8×10^9 Bq ^{57}Co in rhodium matrix (Ritverc GmbH, St. Petersburg) was used at room temperature. Spectra of olivines from pallasites were measured in velocity range of about ±4 mm/s with statistical count rate ranged from ~1.9×10^5 to ~2.4×10^5 counts per channel and the signal-to-noise ratio varied from 63 to 74 in the spectra presented in 4096 channels. Mössbauer spectra of ordinary chondrites were measured in a larger velocity range (±8–10 mm/s). For their analysis, chondrite spectra were converted into 2048 channels by a consequent summation of two neighboring channels. Statistical count rate in the spectra presented in 2048 channels ranged from ~8.1×10^5 to ~4.2×10^6 counts per channel and the signal-to-noise ratio varied from 117 to 220. The spectra were computer fitted with the least squares procedure using UNIVEM-MS program (from the Research Institute of Physics, Southern Federal University, Rostov-on-Don) with a Lorentzian line shape. The spectral parameters such as: isomer shift, δ, quadrupole splitting (quadrupole shift for magnetically split spectra), ΔE_Q, magnetic hyperfine field, H_{eff}, line width, Γ, relative subspectrum area, S, and statistical quality of the fit, χ^2, were determined. An instrumental (systematic) error for each spectrum point was ±0.5 channel (the velocity scale), the instrumental (systematic)

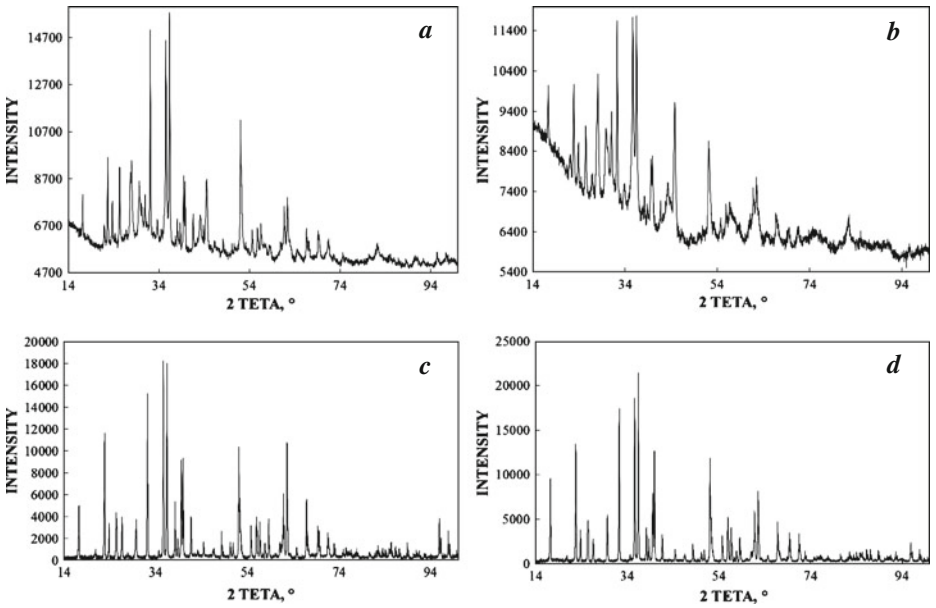

Fig. 1 X-ray diffraction patterns of the powdered samples of Farmington L5 (**a**) and Tsarev L5 (**b**) ordinary chondrites fragments and olivine extracted from Omolon (**c**) and Seymchan (**d**) meteorites

error for the hyperfine parameters was ±1 channel. If an error calculated with the fitting procedure (fitting error) for these parameters exceeded the instrumental (systematic) error we used the larger error instead. Values of δ are given relative to α–Fe at 295 K.

3 Results and discussion

The XRD patterns of Farmington L5, Tsarev L5 and olivines extracted from Omolon and Seymchan are shown in Fig. 1. Their analysis showed that ordinary chondrites have the same phase composition with olivine, pyroxene, troilite and metal phase, however, olivine content in Farmington L5 was found larger than that in Tsarev L5. It was not possible to distinguish peaks related to Fe^{3+} compound in the XRD pattern for Tsarev L5 probably due to their coincidence with other more intensive peaks. The olivine sample extracted from Omolon contains a mixture of three phases: the main phase of $(MgFe)_2SiO_4$ was about 94 wt.%, FeS was about 2 wt.% and SiO_2 was about 4 wt.%. The olivine sample extracted from Seymchan contains two phases: the main phase of $(MgFe)_2SiO_4$ was about 97 wt.% and SiO_2 was about 3 wt.%.

Mössbauer spectra of the Farmington L5 and Tsarev L5 ordinary chondrites were measured at 295 and 90 K and converted into 2048 channels. These spectra consisted of several magnetic sextets and quadrupole doublets corresponding to the main phases in chondrites (the room temperature spectrum of Farmington L5 is shown in Fig. 2a). To fit the room temperature spectra we used one sextet for troilite component, one or two sextets to fit metal phase component, two pairs of quadrupole

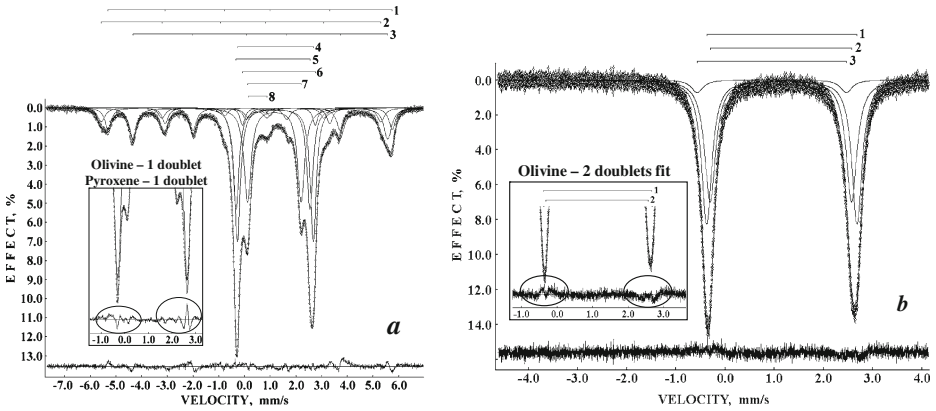

Fig. 2 Mössbauer spectra of Farmington L5 (**a**) and olivine from Seymchan (**b**) measured at 295 K. Indicated components are the result of the best fit. The differential spectra are presented below

doublets were used to fit both olivine and pyroxene components taking into account the ^{57}Fe occupation of the M1 and M2 sites in silicates, and one quadrupole doublet for ferric component. The necessity of two pairs of quadrupole doublets for olivine and pyroxene components fit was confirmed by decrease of χ^2 values and improving of differential spectra in comparison with the fit using one quadrupole doublet for each olivine and pyroxene components. For instance, in the case of the fit of the Farmington L5 spectrum (Fig. 2a) using one doublet for both olivine and pyroxene the value of χ^2 was 7.16 while in the case of the best fit χ^2 was 3.51, a significant improving of differential spectrum is clearly seen in this figure as well. As for olivine subspectra, the quadrupole doublet with larger S was assigned to the ^{57}Fe in the M1 sites while that with smaller S was assigned to the ^{57}Fe in the M2 sites due to well-known fact of slightly larger Fe^{2+} occupancy in the M1 sites of olivine [2].

Mössbauer spectra of olivines extracted from Omolon and Seymchan meteorites look like asymmetric doublets with inverse peaks intensities at 295 and 90 K (see the room temperature spectrum of olivine from Seymchan in Fig. 2b). It was shown earlier [16] that small contribution from the troilite sextet (peaks 3 and 4 were in fact within the noise) in the spectra of olivine extracted from Omolon measured in small velocity range can be neglected. Mössbauer spectra were fitted with several numbers of quadrupole doublets. It should be noted that in the case of extracted olivines the third additional minor component related to the high spin ferrous compound was observed in the spectra of both samples at both temperatures. The necessity of this minor component marked as X was confirmed by comparison of the χ^2 values and differential spectra. For instance, a comparison of two fits of the room temperature Mössbauer spectrum of olivine extracted from Seymchan using two and three quadrupole doublets showed that the χ^2 values were 1.208 (deviation of χ^2 was 9.5 σ) and 1.106 (deviation of χ^2 was 4.8 σ), respectively, and differential spectrum became more linear for the three doublets fit (Fig. 2b). The components of olivine Mössbauer spectra were related to the ^{57}Fe in the M1 and M2 sites in the same way like the spectral components of olivine in ordinary chondrites.

The tendencies of temperature dependences of ΔE_Q for olivines in ordinary chondrites and extracted from pallasites are shown in Fig. 3. The values of ΔE_Q

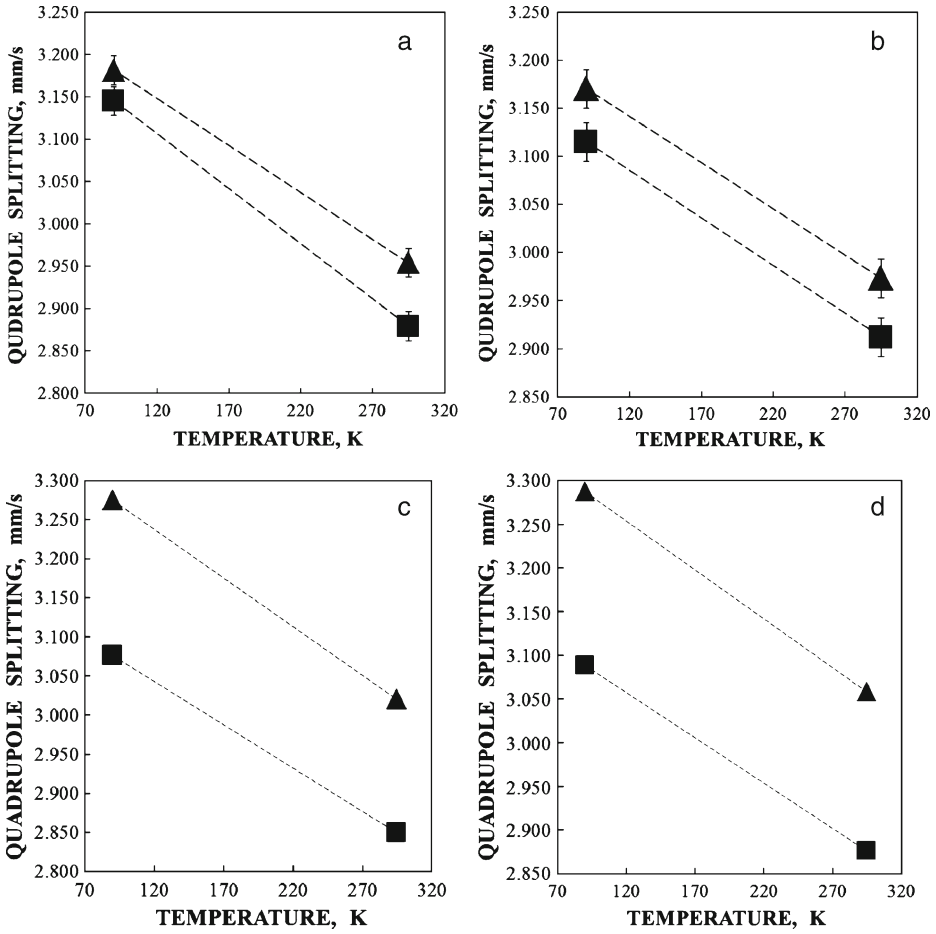

Fig. 3 Tendencies of quadrupole splitting temperature dependences for the ^{57}Fe in the M1 (▲) and M2 (■) sites in meteoritic olivines: Farmington L5 (**a**), Tsarev L5 (**b**), Omolon (**c**) and Seymchan (**d**)

for the ^{57}Fe in the both M1 and M2 sites in the studied olivines characterize the high spin ferrous iron. Therefore, an increase of the electric field gradient with temperature decrease may be related to the presence of the low-lying electron terms which produce the electric field gradient with opposite sign than the ground one. It was interesting that the difference between ΔE_Q values for the ^{57}Fe in the M1 and M2 sites of olivines in Farmington L5 and Tsarev L5 chondrites was significantly less than that for the ^{57}Fe in the M1 and M2 sites of olivines extracted from Omolon and Seymchan pallasites. This finding indicates that Fe^{2+} microenvironment for the M1 and M2 sites of olivines in ordinary chondrites has less difference than that of olivines extracted from pallasites. Thus, the local environment in the M1 and M2 sites may vary in olivines with different origin.

4 Conclusion

A comparative study of olivines in two bulk ordinary chondrites and extracted from two pallasites using Mössbauer spectroscopy with a high velocity resolution demonstrated differences of quadrupole splitting for the ^{57}Fe in both the M1 and M2 sites of studied olivines. These differences are related to the small variations in each site microenvironment probably due to different origin of each olivine.

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